

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 02 APR 2004

WIPO PCT



Applicant's or agent's file reference C4195(C)/sje		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 02/13959	International filing date (day/month/year) 10.12.2002	Priority date (day/month/year) 18.01.2002	
International Patent Classification (IPC) or both national classification and IPC C08F20/34			
Applicant UNILEVER PLC			

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 9 sheets.

- This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 28.07.2003	Date of completion of this report 01.04.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Clement, S Telephone No. +49 89 2399-8512 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 02/13959

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-3, 10, 12-29 as originally filed
4-9, 11 received on 22.01.2004 with letter of 19.01.2004

Claims, Numbers

8-11 as originally filed
1-7 received on 22.01.2004 with letter of 19.01.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form..
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP 02/13959**

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-11
	No: Claims	
Inventive step (IS)	Yes: Claims	1-11
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-11
	No: Claims	

2. Citations and explanations

see separate sheet

Ad Section V:

Neuheit:

WO 93/13142 discloses an ungelled reaction product prepared from carboxylic acid group containing polymeric material (e.g. acrylic acid/t.-butylaminoethyl methacrylate) and an azetidinol containing compound which may also be polymeric (page 6). The reaction product contains a hydroxy aminoalkyl ester and is not capable of self-crosslinking. The reaction product is suitable as a film former in preparing coating compositions e.g. for cloths (abstract, page 8, lines 18-25, page 10, lines 12-13). WO'142 does not disclose azetidinium functionalized polymers.

WO 93/13063 describes a polyazetidinol containing material which is prepared from a polyamine (e.g. bis-4-(aminocyclohexyl)methane) and epihalohydrin. The material is capable of self-crosslinking and may be reacted with a polycarboxylic acid polymer. The resulting product is suitable as a film former in preparing coatings on cloth (claims, page 4, page 7, lines 25-27). Azetidinium functionalized polymers are not obtained.

US-A-3,705,076 deals with aminoester modified vinyl addition polymers (methylmethacrylate/methacrylic acid ester copolymers) useful as clear coating compositions for metal or wood (abstract). No azetidinium functionalized polymers are mentioned.

DE-A-1 258 604 concerns a process for preparing crosslinked polymers obtained by reacting amino-group containing polymers with oligomeric compounds containing N-acyl- β -lactam groups (e.g. N,N'-terephthaloyl-bis-(4,4-dimethyl-azetidin-2-on)). DE'604 does not teach azetidinium functionalized polymers.

US-A-3,702,799 teaches polymers of quaternary ammonium compounds used as wet strength agents in paper. The polymer is obtained by reacting epihalohydrin with a polymer containing tertiary amino-groups. US'799 neither relates to acetidinium functionalized polymers nor to polymers containing secondary amine groups.

WO 99/54541 describes a composition for textile printing comprising a copolymer of polymerized units of an azetidinium monomer and units of a guanidine monomer. The amino groups of the polymerized guanidine units are not regarded as secondary amine

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP02/13959

groups.

EP-A-0 016 623 discloses polymeric wet strength additives obtained by reacting epihalohydrin with a polymer formed of tertiary amine-group containing monomer units. EP'623 does not mention azetidinium functional polymers containing secondary amine groups.

EP-A-0 403 336 discloses coatings for wool comprising microparticles of an acrylic polymer, the surface of which consists of a copolymer comprising units of N-alkyl azetidine methacrylate. The azetidine functionalized polymers according to EP'336 do not contain amino groups at all.

Therefore, the subject-matter of present claims 1-11 is novel over the prior art cited in the international search report (Art. 33 (2) PCT).

Inventive Step

None of the documents cited in the international search report suggests the azetidinium functionalized polymer containing secondary amine groups as claimed in order to provide a textile treatment composition which imparts improved wear resistance, reduced pilling, improved colour definition, reduced wrinkling and improved perfume longevity.

Thus, the subject-matter of the present claims 1-11 involve an inventive step (Art. 33 (3) PCT).

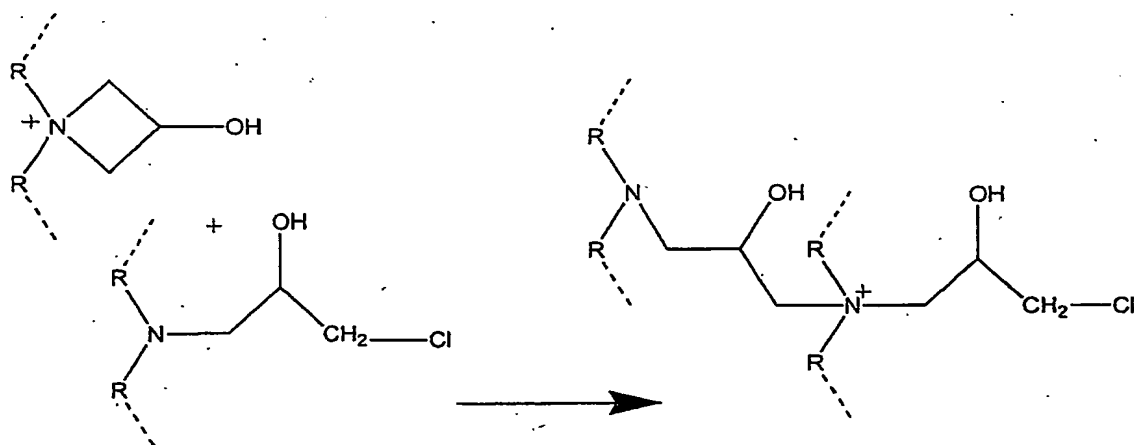
Industrial applicability

The subject-matter of present claims 1-11 fulfill the requirements of Art. (33 (4) PCT).

- 4 -

link and hence become tertiary. The consequence of this is that there are no secondary amines remaining in the polymer after the epichlorohydrin treatment.

- 5 During the internal cross-linking reaction between an azetidinium group and a gamma chlorohydrin the azetidinium ring opens leaving a tertiary nitrogen but the corresponding chlorohydrin is converted to a cationic, quaternary group. Thus the overall charge on the polymer is unchanged.
- 10 The mechanism is illustrated below.



15

Brief Description of the Invention

We have determined that improved textile treatment polymers can be made which have secondary nitrogen atoms available for a cross-linking reaction with the azetidinium group.

20

- 5 -

Accordingly, the first aspect of the invention comprises an azetidinium functionalised polymer containing secondary amine groups.

5 Cross-linking reactions between the azetidinium group and primary amine groups does not form quaternary groups and consequently does not result in a charged, cross-linked polymer. This lack of charge is believed to substantially reduce the problems of stain fixing and dye adsorption. In
10 the context of the present invention the term 'amine' does not include amides.

Particular benefits are obtained if the polymer is synthesised from acrylate-functional monomers, thereby
15 allowing further functionality to be incorporated into the polymer.

Accordingly, a second aspect of the present invention subsists in a azetidinium functionalised polymer of which
20 the monomers comprise:

- a) an amino-acrylate and/or amino-alkacrylate monomer, and,
- 25 b) optionally, further non-amino acrylate and/or alkacrylate monomer.

Typically, the polymers are epihalohydrin modified to form azetidinium groups.

30

- 6 -

A third aspect of the present invention provides a textile treatment composition which comprises an azetidinium functionalised polymer in accordance with the first or second aspect of the invention and a textile compatible carrier.

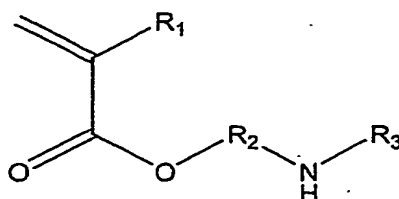
Typical concentrations of the polymers according to the invention in the final product will be such as to give 0.01-1%wt, preferably 0.1-0.2%wt on weight of textile material being treated. Typically products will contain 0.5-10%wt of polymer on product.

Detailed Description of the Invention

The polymer is preferably synthesised from an amine-containing acrylate or alkyl-acrylate monomer, with or without other monomers which do not contain an amine. Polymers formed from these monomers have pendant secondary amine groups. These polymers can then be modified (e.g. with epichlorohydrin) to give the azetidinium functionality.

The amine-containing polymers:

The preferred amine/acrylate monomers have the general structure given below:



- 7 -

where

R_1 is hydrogen or a C_1 - C_6 alkyl,

R_2 is C_1 - C_6 , alkyl, alkoxy or repeating units thereof,
typically C_2 alkyl, and,

5 R_3 is C_1 - C_6 alkyl, alkoxy or repeating units thereof

Typically, R_1 will be hydrogen or methyl, i.e. the monomer
will be an acrylate or methacrylate. Typically R_2 will be a
two-carbon unit. While the substituents R_2 and R_3 can

10 comprise alkoxy repeat units, such as glycol ether it is
preferable that both are saturated alkyl chains. These alkyl
chains may be linear or branched.

These polymers can be reacted in the normal manner to give
15 polyacrylate polymers.

- 8 -

A suitable monomer is 2-(tert-butylamino)ethyl methacrylate. In this case R1 is methyl, R2 is ethyl and R3 is t-butyl. In this case the pendant amines will be secondary.

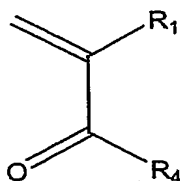
- 5 The polymer can be synthesised from a single type of amine-containing monomer or from a mixture of monomers of different structures.

Non-amine acrylate monomers:

10

Choice of the other (non-amine) monomers enables additional functionality to be added to the polymers. Preferred added functionality includes one or more of improved water solubility, the ability to confer softness to a textile and/or stain/soil repellence. Preferably, the monomers will be of the general formula given below:

15



20 Where:

R1 is hydrogen or a C1-C6 alkyl, alkoxy or repeat units thereof

R4 is a functional group does not contain an amine.

- 9 -

R₁ will typically be hydrogen or methyl, i.e. the monomer will be an acrylate or methacrylate.

By varying R₄ it is possible to modify the features of the
5 polymer.

When the R₄ group is polar, such as a polyalkylene glycol, the polymer is more water soluble.

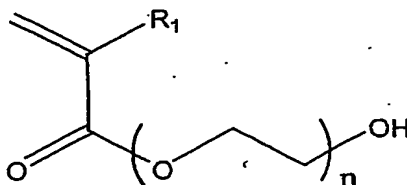
10 When the R₄ group is oily, such as a silicone/siloxane or a fatty chain, the polymer has softening properties.

When the R₄ group is relatively unreactive, such as a fluorocarbon the polymer confers stain and soil repellence
15 properties.

Mixture of non-amine monomers may be employed to give some or all of these features. Non-limiting examples of suitable monomers are given below.

20

For water-soluble polymers R₄ can be poly(ethyleneglycol) and typical monomers are poly(ethyleneglycol) (meth)acrylates, of the general structure given below:



25

- 11 -

amines and azetidinium groups which are capable of cross linking.

The preferred level of epihalohydrin used is determined by
 5 the type of amine present. For secondary amines no more than
 a half-molar equivalent of epihalohydrin is used. Slightly
 higher levels of epihalohydrin can be used, preferably no
 more than 5%, although with higher levels tertiary amines
 will be formed. Lower levels will lead to a lower degree of
 10 modification and less effective cross-linking.

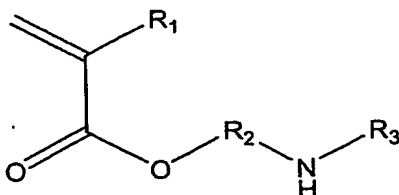
Carriers and Product Form:

15 The compositions of this invention, when applied to a
 fabric, may be cured by a domestic curing step including
 ironing and/or tumble drying, preferably tumble drying.
 Preferably, these curing steps are carried out at
 temperatures in the range 60 to 100°C, more preferably from
 20 80 to 100°C.

The compositions of the invention may be used before, during
 or after a conventional laundry process and are preferably
 packaged and labelled as such. The laundry process includes
 25 large and small processes, and is preferably a domestic
 process.

CLAIMS

1. An azetidinium functionalised polymer containing secondary amine groups.
- 5 2. An azetidinium functionalised polymer according to claim 1 of which the monomers comprise:
 - 10 a) an amino-acrylate and/or amino-alkacrylate monomer, and,
 - b) optionally, further non-amino acrylate and/or alkacrylate monomers.
- 15 3. A textile treatment composition which comprises a polymer in accordance with claim 1 or claim 2 and a textile compatible carrier.
- 20 4. A textile treatment composition according to claim 3 wherein the concentration of the polymer is such as to give 0.01-1%wt on weight of textile material being treated.
- 25 5. A polymer according to claim 2 wherein the amine containing acrylate monomers have the general structure:



- 30 -

wherein

R₁ is hydrogen or a C₁-C₆ alkyl,

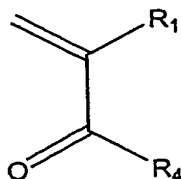
R₂ is C₁-C₆, alkyl, alkoxy or repeating units thereof,
and,

5 R₃ is C₁-C₆ alkyl, alkoxy or repeating units thereof.

6. A polymer according to claim 5 wherein the amine
containing acrylate monomers include one or more of 2-
Aminoethyl methacrylate, and, 2-(tert-butylamino)ethyl
10 methacrylate.

7. A polymer according to claim 2 wherein the non-amino
acrylate and/or alkacrylate monomers are of the general
formula:

15



where:

20 R₁ is hydrogen or a C₁-C₆ alkyl, alkoxy or repeat units
thereof,

R₄ is a functional group does not contain an amine.